

POLYMER NANOCOMPOSITES CONTAINING POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

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Introduction

Polyhedral oligomeric silsesquioxanes (POSS)¹ are being examined for use in many applications. These applications include space-survivable coatings,^{2,4} and ablative and fire-resistant materials.^{5,9} POSS compounds have a rigid, inorganic core and have been produced with a wide range of organic functionality. Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, often improving both thermal and mechanical properties. Herein, we describe the preparation and properties of POSS compounds and their polymer nanocomposites.

Polymeric materials are typically tough, lightweight, and easy to process. However, they often lack resistance to oxidation and degrade at high temperatures. Ceramic materials, on the other hand, are thermally stable and have high oxidative resistance, but are brittle and difficult to process. POSS materials contain a thermally robust inorganic core that are surrounded by an organic corona (figure 1), which increases miscibility in the polymer. POSS have been incorporated into many polymer systems in order to improve the polymer thermo-oxidative stability.

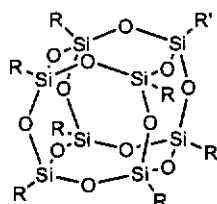


Figure 1. Polyhedral oligomeric silsesquioxanes (POSS). (R = nonreactive organic group for polymer compatibility, R' = R or reactive group for copolymerization or grafting.

POSS are typically produced by the acid- or base-catalyzed hydrolysis of trifunctional silanes (figure 2). POSS compounds can be produced as either completely or incompletely condensed cage structures. The completely condensed compounds may contain cages with six to twelve silicon atoms, although T₆ and T₁₂ cages can be prepared selectively. Incompletely condensed cages typically contain four to eight silicon atoms and still retain reactive silanol groups. The yields for these reactions are often nearly quantitative. The typical reaction byproduct is an ill-defined resinous material that is formed when the condensation is less controlled. This resin may contain partial cage structures and ladder structures, etc. Fortunately, the resin is typically soluble, allowing its removal by extraction in various solvents.

RSiX₃ acid or base hydrolysis →

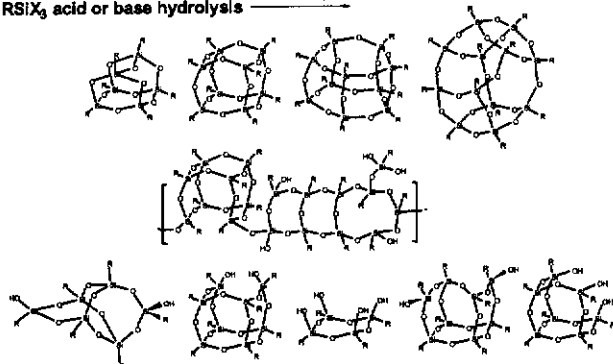


Figure 2. POSS synthesis involves the acid- or base-catalyzed hydrolysis of trifunctional silanes to produce inorganic-organic hybrid materials.

Results and Discussion

POSS compounds are typically used to improve the thermal and mechanical properties of polymers. This is often done by the blending of completely condensed POSS cages into polymers in which they are miscible. Thermal properties of the POSS compounds are quite important because many polymers have high melt-processing temperatures. The POSS compound to be blended into the polymer must not only be highly miscible in the polymer but must be thermally stable beyond the polymer processing temperature. Fortunately, POSS compounds volatilize or degrade at temperatures up to 400 °C. This high temperature stability allows the blending of many of these POSS compounds to improve properties of various polymer systems.

In addition to melt-blending, POSS can be chemically bound to the polymer backbone (figure 3). This is usually done one of two ways. The first method involves the direct copolymerization of POSS monomers during polymerization. This has been done in both step-growth and chain-growth polymerizations. The second method for binding POSS to the polymer backbone involves the chemical modification of preformed polymers and results in the POSS being pendant to the polymer backbone. It has been observed that pendant POSS produce superior thermal properties of the polymers to which they are attached when compared to similar polymers with POSS in the polymer backbone.

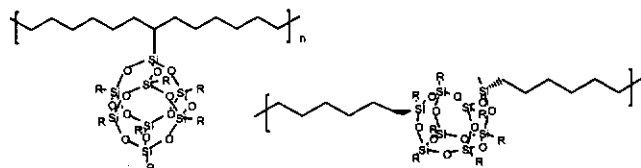


Figure 3. Generic polymer architecture with POSS included by (a) grafting or chain-growth polymerization or (b) step-growth polymerization.

Many POSS compounds are commercially available.¹ The use of these and other POSS compounds in various polymer systems will be discussed.

Conclusion

Polyhedral oligomeric silsesquioxanes (POSS) contain inorganic cores with organic coronae to provide polymer miscibility. They may also possess reactive groups for polymer grafting or copolymerization. These compounds have been produced by the acid- or base-catalyzed hydrolysis of trifunctional monomers to produce both completely and incompletely condensed cage structures. POSS have been incorporated into both organic and inorganic polymers and shown to improve both thermal and mechanical properties.

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